



# Selective sensing of copper and mercury ions with pyrene-functionalized fluorescent film sensor containing a hydrophilic spacer

Yuan Cao, Liping Ding\*, Wenting Hu, Lin Wang, Yu Fang<sup>1</sup>

Key Laboratory of Applied Surface and Colloid Chemistry of Ministry of Education, School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an, 710062, PR China

## ARTICLE INFO

### Article history:

Received 7 October 2012

Received in revised form 27 January 2013

Accepted 12 February 2013

Available online 26 February 2013

### Keywords:

Fluorescence

Sensor

Film

Self-assembled monolayer

Metal ions

## ABSTRACT

A fluorescent film sensor for Cu(II) and Hg(II) ions was designed and prepared by chemical attaching pyrene moieties on an epoxy-terminated surface via a long flexible and hydrophilic spacer. The chemical attachment of pyrene moieties on the surface was verified by contact angle, XPS, and fluorescence characterization. The fluorescence responses of the present film to a series of metal ions in aqueous solution indicate that this film sensor is sensitive to both copper and mercury ions. Presence of other metal ions, including Ni(II), Fe(III), Pb(II), Mg(II), Ba(II), Zn(II), La(II) and Eu(II), has little effect upon the fluorescence emission of the film. The sensitivity of the present film sensor is quite high toward both Cu(II) and Hg(II) ions in the form of inorganic salts as revealed by the large  $K_{SV}$  values. Moreover, the presence of organic anions produces little influence on the sensitivity of the film sensor toward metal ions, suggesting the introduction of the hydrophilic spacer weakens the spacer layer screening effect in aqueous solution. The novel fluorescent film sensor may have potentials as Cu(II) and Hg(II) sensors to probe natural environments.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

Protection and conservation of water resources, preventing contamination from anthropogenic as well as natural sources, is an important task to human. Among the inorganic contaminants, heavy metal ions play an important role and may also have intrinsic risks due to their potential impact on human health and environment [1]. Long-term exposure to or excessive intakes of heavy metal ions (e.g. Hg(II), Cu(II), Pb(II), Cd(II), Cr(VI), Ni(II), etc.) will cause disruption of nervous system and immune system, bring damages to brain function and fails other organs like heart, kidney and lungs [2]. Moreover, many heavy metals are carcinogens. Therefore it is in urgent need of developing highly sensitive and selective sensors to detect heavy metal ions particularly in aqueous phase [3,4].

Fluorescent chemical sensors have received a great deal attention due to the advantages in terms of sensitivity, selectivity, no need of references, and multiple readout signals, when compared with electrochemical and other optical sensors [5]. Most of the reported fluorescent chemical sensors for heavy metal ions are

solution-used ones [6,7]. By comparison, fluorescent film sensors with fluorophores chemically attached on solid surfaces offer additional advantages such as long-term stability, reversibility, and device implementation and miniaturization [8]. Self-assembled monolayers (SAMs) of  $\omega$ -functionalized organosilanes have been widely used to produce functional surfaces for chemical attaching fluorophores [9] and thereby to construct film sensors [10–12]. In 2001, Crego-Calama and Reinhoudt reported their pioneer work of constructing fluorescent SAM film sensors for heavy metal ions, where they employed  $\text{NH}_2$ -terminated SAMs to chemically immobilize dansyl and coumarin moieties and realized fluorescent film sensors for  $\text{Pb}^{2+}$  ions in acetonitrile solution [13]. A unique feature of fluorescent SAM sensor for metal ions is there is no particular need of introducing receptor molecules, where the functional subunits in the spacer connecting the solid surface and the reporting fluorophores are involved in the sensing process [11,13]. Our group used epoxy-terminated SAMs to immobilize small fluorophores (pyrene, dansyl, and anthracene, etc.) and have constructed a series of fluorescent SAM film sensors for Cu(II) ions in aqueous solution [11,14,15]. Besides small fluorophores, fluorescent conjugated polymers have also been used to build fluorescent SAM film sensors for metal ions such as Cu(II) [16] and Fe(III) ions [17]. However, the categories of metal ions can be detected by fluorescent SAM sensors are very limited up to now. It is highly desirable to develop such film sensors for other metal ions.

\* Corresponding author. Tel.: +86 29 81530790; fax: +86 29 81530727.

E-mail addresses: [dinglp33@snnu.edu.cn](mailto:dinglp33@snnu.edu.cn) (L. Ding), [yfang@snnu.edu.cn](mailto:yfang@snnu.edu.cn) (Y. Fang).

<sup>1</sup> Tel.: +86 29 81530790; fax: +86 29 81530727.

In our previous reports about fluorescent SAM film sensors for metal ions, we found that not only the functional subunits in the spacer but also the flexibility and the polarity of the spacer play a role in the recognition process [14,18]. When a long flexible hydrophobic spacer is used, the spacer tends to form compact conformation in aqueous solution and yield a hydrophobic spacer layer with fluorophores embedded inside. This hydrophobic spacer layer blocks inorganic anions from accessing surface fluorophores. On the contrary, organic anions have a better chance entering the hydrophobic spacer layer and draw metal ions close to fluorophores due to electrostatic interaction. Therefore, these types of film sensors exhibit a lower sensitivity toward inorganic copper salts than the organic ones due to the screening effect of the spacer layer on inorganic anions [14,18]. Since many metal ions exist in the nature in the form of inorganic salts, it is more significant to develop film sensors possessing a high sensitivity toward heavy metal ions with inorganic anions. In order to improve the sensitivity of such film sensors for inorganic metal ions, hydrophilic spacers are desirable to connect fluorophore and solid surface, where loose conformation may form and the probability of fluorophores exposed to the testing metal ions may be increased.

Herein, a pyrene-functionalized fluorescent SAM film sensor with a hydrophilic spacer containing oligo(oxyethylene) unit was specially designed and prepared. Pyrene was selected as the reporting units due to its high quantum yield and easy derivatization. It was derived with  $\alpha,\omega$ -diamino oligo(oxyethylene) to yield an amine-functionalized pyrene derivative, which was then reacted with the epoxy-terminated SAM and generated the resulting film sensor. The diamine-linked oligo(oxyethylene) subunits in the spacer provide not only the hydrophilic properties but also the affinity toward mercury ion [19,20]. As expected, the present film sensor exhibits admirable sensitivity and selectivity toward Cu(II) and Hg(II) ions in aqueous solution.

## 2. Material and methods

### 2.1. Materials

4,7,10-Trioxa-1,13-tridecanediamine (Sigma–Aldrich, 98%), pyrene (Alfa, 98%), 3-glycidoxypropyltrimethoxysilane (GPTS; Acros, 97%) were used as received. Pyrenesulfonyl chloride (PSC) was synthesized by adopting a literature method [21].  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{Cu}(\text{Ac})_2$ ,  $\text{CuSO}_4$ ,  $\text{CuCl}_2$ ,  $\text{HgCl}_2$ ,  $\text{Ni}(\text{NO}_3)_2$ ,  $\text{Fe}(\text{NO}_3)_3$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{Zn}(\text{NO}_3)_2$ ,  $\text{LaCl}_3$ , and  $\text{EuCl}_3$  were of at least analytical grade. Toluene is distilled over sodium under nitrogen prior to use. Trichloromethane is dried with anhydrous  $\text{CaCl}_2$  overnight before use. Aqueous solutions were prepared from Milli-Q water (18.2 M $\Omega$  cm at 25 °C). All other reagents are analytically pure. Glass substrates used for fabrication of SAM films are microscope slides with size of  $\sim 0.9 \times 2.5$  cm.

### 2.2. Methods

Fluorescence measurements were performed at room temperature on a time-correlated single photon counting Edinburgh FLS 920 fluorescence spectrometer with a front-face method. The fabricated film was first inserted into a quartz cuvette fixed on the solid sample holder and its surface was put facing the excitation light source. Then, 2.5 mL of water was added to the cuvette. After recording the original fluorescence emission of the film, a given volume of the standard aqueous solution of the tested metal ion was added with stirring. Finally, the fluorescence emission spectrum of the system in the presence of metal ions was recorded. The position of the film was kept constant during each set of measurements. Contact angles of the films were measured on a video-based

contact angle measuring device SCA20. X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCAPHI5400 photoelectron spectrometer.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were measured on Bruker AV 400 MHz NMR spectrometers. The high resolution mass spectra (MS) were acquired in ESI positive mode using Bruker maxis UHR-TOF Mass Spectrometer. The FTIR spectra were measured on a Fourier Transform Infrared Spectrometer (Vertex 70v, Bruker, Germany).

### 2.3. Synthesis of *N*-(3-(2-(2-(3-aminopropoxy)ethoxy)ethoxy)propyl)pyrene-1-sulfonamide (Py-TOA)

The diamine derivative of pyrene containing oligo(oxyethylene) as a linker, Py-TOA, was synthesized by reacting PSC with the  $\alpha,\omega$ -diamine compound, 3,3'-((oxybis(ethane-2,1-diyl))-bis(oxy))-bis(propan-1-amine) (TOA). The synthesis procedure is as follows: A solution of PSC (150 mg, 0.5 mmol) in  $\text{CHCl}_3$  (50 mL) was added dropwise to a solution of TOA (1 mL, 5 mmol) in  $\text{CHCl}_3$  (50 mL) at 0 °C under stirring at  $\text{N}_2$  atmosphere over a period of 8 h, after which the reaction system was stirred at room temperature for an extra hour. Then the mixture was washed with brine until the pH of the aqueous layer is neutral. Organic layers were combined and dried with anhydrous  $\text{Na}_2\text{SO}_4$  overnight and filtered. The resulting yellow-green oil was purified by column chromatography on silica gel column with  $\text{CH}_2\text{Cl}_2$ :  $\text{CH}_3\text{OH}$  (*v*:*v*, 20:1) as eluent. Py-TOA was obtained as a pale yellow solid after freeze-drying (150 mg, 62%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.03 (d, *J*=9.4 Hz, 1H, Ar H), 8.67 (d, *J*=8.2 Hz, 1H, Ar H), 8.27–8.02 (m, 7H, Ar H), 4.31 (s, 2H,  $\text{NH}_2$ ), 3.57–3.37 (m, 12H), 3.04 (t, *J*=36.4 Hz, 2H,  $\text{CH}_2$ ), 2.90 (t, *J*=6.2 Hz, 2H,  $\text{CH}_2$ ), 1.77 (t, *J*=12.1 Hz, 2H), 1.61 (d, *J*=5.9 Hz, 2H,  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 134.54 (C4, Ar C), 131.94 (C4, Ar C), 130.91 (C4, Ar C), 130.19 (C4, Ar C), 129.91 (CH, Ar C), 129.78 (C4, Ar C), 128.02 (CH, Ar C), 127.30 (CH, Ar C), 127.02 (CH, Ar C), 126.71 (CH, Ar C), 126.66 (CH, Ar C), 125.16 (C4, Ar C), 124.04 (CH, Ar C), 123.79 (CH, Ar C), 123.61 (CH, Ar C), 77.37 (C4, Ar C), 77.05 ( $\text{CH}_2$ ), 76.74 ( $\text{CH}_2$ ), 70.41 ( $\text{CH}_2$ ), 70.00 ( $\text{CH}_2$ ), 69.67 ( $\text{CH}_2$ ), 69.35 ( $\text{CH}_2$ ), 41.42 ( $\text{CH}_2$ ), 39.72 ( $\text{CH}_2$ ), 31.14 ( $\text{CH}_2$ ), 28.87 ( $\text{CH}_2$ ). FTIR (KBr plate,  $\text{cm}^{-1}$ ): 3437 ( $-\text{NH}_2$ ), 3284 ( $-\text{NH}$ ), 3048 (Ar–H), 2923 ( $-\text{CH}_2$ ), 1588 (Ar C=C), 1094 ( $-\text{C}-\text{O}-\text{C}$ ). MS (ESI, *m/z*):  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{26}\text{H}_{32}\text{N}_2\text{O}_5\text{S}$ , 485.2116; found, 485.2117. The  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, FTIR and MS spectra are provided in the Supporting Information.

### 2.4. Preparation of Py-TOA-modified SAM film (film Py-TOA)

The originally ethanol-cleaned glass slides (**S1**) was treated in a freshly prepared “piranha solution” (7/3, *v/v*, 98% $\text{H}_2\text{SO}_4$ /30% $\text{H}_2\text{O}_2$ ) (warning: piranha solution should be handled with extreme caution since it can react violently with organic matter) for 1 h, then rinsed thoroughly with plenty of water after the “piranha solution” cooled to room temperature, and dried with  $\text{N}_2$  flow. The activated glass slide was immersed in 50 mL of toluene solution of GPTS (0.6%, *V/V*), containing 20  $\mu\text{L}$  of water, for 12 h at 50 °C. After this, the glass slide was rinsed with toluene and chloroform, successively, to remove any physisorbed organosilanes.

The GPTS-covered glass slide was further macerated into the chloroform solution of Py-TOA (6 mM) and then refluxed for 24 h. Pyrene moieties were expected to be chemically bound to the glass surface via the amine groups of Py-TOA reacting with the epoxy termini of SAM. To remove those unreacted Py-TOA, the fabricated functionalized surfaces were rinsed thoroughly with chloroform, ethanol and water, successively. The synthesis of Py-TOA and its coupling onto glass surface is schematically shown in Scheme 1.

Download English Version:

<https://daneshyari.com/en/article/5354504>

Download Persian Version:

<https://daneshyari.com/article/5354504>

[Daneshyari.com](https://daneshyari.com)